

Pressure Effect on the Magnetic Phase Transition of Guest-tunable Weak Ferromagnets [Fe{N(CN)₂}₂(pyrimidine)](guest) (Guest = Ethanol and Pyrimidine)

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The spontaneous magnetization of [Fe{N(CN)₂}₂(pm)]-(ethanol) (pm = pyrimidine) was suppressed under pressure up to 0.5 GPa and finally behaved as a paramagnet at 0.6 GPa. The loose packing of the host-guest complex structure seems responsible for the pressure-sensitive magnetism. On the other hand, [Fe{N(CN)₂}₂(pm)](pm) exhibited relatively small pressure dependence of the phase transition behavior.

There have been numerous reports on infinite metal-organic polymeric frameworks which attract attention for nanoporous materials providing potential applications in many areas (gas absorption for instance)¹ and also for supramolecular chemistry controlling their physical properties.^{2,3} We have already reported the self-assembled transition-metal complexes containing both pyrimidine (pm) and N(CN)₂⁻ bridges, namely, [M^{II}{N(CN)₂}₂(pm)] (M = Fe, Co), which exhibit a pillared-layer structure (Figure 1) and weak ferromagnetism (canted antiferromagnetism).⁴ The metal dicyanamides⁵ and related mixed-ligand systems^{6,7} have often been characterized as weak ferromagnets. The [M{N(CN)₂}₂(pm)] skeleton has been clarified to work as a host.⁸ We examined the guest-dependence of the magnetic properties for the "solvated magnets" of [M{N(CN)₂}₂(pm)], and the magnetic phase transition phenomena were drastically changed depending on the guest molecules; for example, *T_N*'s are 3.3 and 5.6 K for [Fe{N(CN)₂}₂(pm)]-(guest) where the guest is ethanol (**1**) or pm (**2**).^{8,9} The origin of the guest-dependence was suggested to be the delicate coordination geometry changes.⁹ Viewing from the mechanical softness of the host-guest systems, we planned to investigate changes of the magnetic properties of **1** and **2** by applying external pressure. Their crystal structures and magnetic properties at ambient pressure were well defined.^{4,9}

Dc magnetic moments of polycrystalline samples of **1** and **2** were measured on a Quantum Design MPMS SQUID magnetometer equipped with a 7 T coil in a temperature range down to 1.8 K. We used a Cu-Be clamp-type cylinder cell¹⁰ fabricated

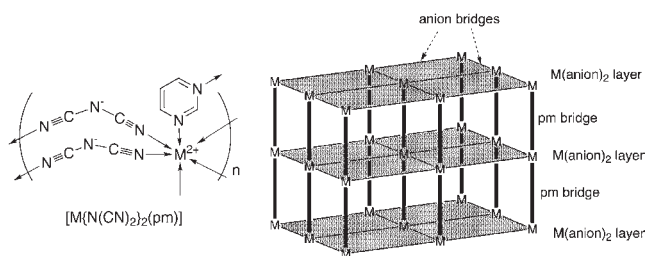


Figure 1. Structural formula and schematic drawing of the crystal of [Fe{N(CN)₂}₂(pm)].

by ElectroLAB (Japan). The pressure medium was Idemitsu daphne oil.¹¹ The applied hydrostatic pressure was calibrated in situ by the pressure dependence of the Pb superconducting transition temperature.¹² Compounds **1** and **2** were prepared according to the reported method.^{4,8} The polycrystalline specimens of 1–2 mg were mounted in the cell and the precise mass was calculated by comparison with the molar magnetization and susceptibility values reported previously.

Figure 2 shows the pressure dependence of the field-cooled magnetization (FCM) of **1**. At ambient pressure the FCM curve started an upsurge near 3.5 K, which reproduced well the reported phase transition temperature of 3.3 K. The upsurge became ambiguous with an increase of the applied pressure and disappeared at 0.47 GPa. This behavior does not imply loss of magnetic phase transition, but the decrease of the spin-canting angle to give a genuine antiferromagnet, as indicated by the magnetization curves under the same pressure. Figure 3 shows the pressure dependence of magnetization curves for **1**. Stepwise saturation behavior was observed at a low pressure region, the origin of

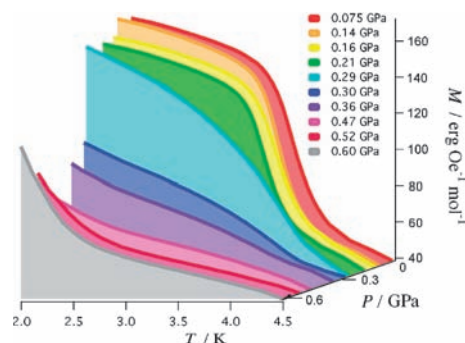


Figure 2. Pressure dependence of the field-cooled magnetization of [Fe{N(CN)₂}₂(pm)](ethanol) (**1**) measured at 5 Oe.

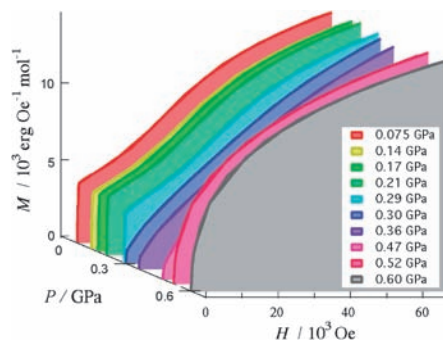


Figure 3. Pressure dependence of magnetization curves of [Fe{N(CN)₂}₂(pm)](ethanol) (**1**) measured at 1.8 K.

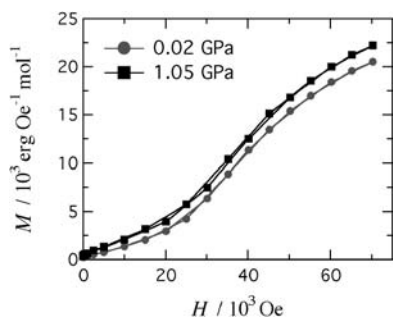


Figure 4. Magnetization curves of $[\text{Fe}\{\text{N}(\text{CN})_2\}_2(\text{pm})](\text{pm})$ (**2**) measured at 1.8 K.

which can be proposed as spin-flip transition from a canted antiferromagnetic phase to a canted ferromagnetic phase.⁹ The spontaneous magnetization was found to be ca. $3 \times 10^3 \text{ erg Oe}^{-1} \text{ mol}^{-1}$ at ambient pressure and decreased with an increase of pressure, being in good agreement of the FCM results. The curves at 0.30 and 0.36 GPa were approximately linear and fell significantly below the data measured under ambient pressure, indicating that this phase is antiferromagnetic. Under the pressure above 0.5 GPa, the FCM curve gradually increased below ca. 2.5 K. The M – H curves at $P > 0.5$ GPa showed a significant convex like a Brillouin function typical of a paramagnet, suggesting that the antiferromagnetic order was lost or shifted to lower temperatures than 1.8 K. Further pressurization up to 1 GPa gave no appreciable effect on the magnetism. After the pressure was removed, we confirmed that the structure of **1** was not broken as evidenced by restoring the initial data in the FCM and M – H measurements.

Similar experiments on **2** were carried out, and we found that the magnetic phase transition and spontaneous magnetization were relatively insensitive to the pressure applied. The stepwise behavior of the magnetization saturation remained and almost unchanged up to 1.05 GPa (Figure 4). The (canted) antiferromagnetic transition temperature of **2** was found to be 5.6 K at ambient pressure as expected from literature⁹ and only slightly elevated to 5.8 K at 1.05 GPa. The opposite trends of the pressure dependence between **1** and **2** can be rationalized from the different magnetic structures of **1** and **2**. The magnetization easy and hard axes are different to each other, despite of almost the same structure of the host skeletons, probably owing to the different single-ion anisotropy.⁹

The crystal structure analysis of **1** revealed the presence of severe disorder of the guest molecules as well as the dicyanamide bridges.⁴ The loose packing of the host–guest complex structure allowing deformation of the crystal structure under pressure seems responsible for the pressure-sensitive magnetism. On the other hand, the guest pm in **2** has a rigid configuration in the void space.⁹ Furthermore, the host dicyanamide skeleton showed no disorder, suggesting the tight packing in the host–guest complex. Accordingly, **2** may stand against deformation under pressure and show no appreciable pressure dependence. The specimen **1** can be regarded as a piezo-switchable magnet; the magnetization was lost and recovered, depending

on the on- and off-states of the external pressure.

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